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Among several CNT samples we tested, the best performance result we have achieved is with metallic SWNT (m-SWNT) coated on PEN (poly-ethylene-naphthalate) transparent composite film: it gave conductivity of 130/sq with 80% transmittance at 400-700nm wavelength range. In contrast,, current commercially available single side inorganic, brittle ITO coated PET film gave 88/sq with 80% transmittance. Our sample mentioned above was prepared with double side coating using a dipping method.

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NOVEL CONDUCTIVE COATINGS OF CARBON NANOTUBES: A FUNDAMENTAL STUDY

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NOVEL CONDUCTIVE COATINGS OF CARBON NANOTUBES: A FUNDAMENTAL STUDY

Research Objectives:

Our primary objective is to find candidate CNT based coatings to achieve high electrical conductivity along with the coatings' high transparency at 400-700nm wavelength range once coated on flexible transparent substrate. Secondary objective is to uncover the fundamentals associated with adhesion of the coating to the surface of the substrate. Third objective is to fabricate sample electronic devices with CNT coated substrate to test its potential commercial applications as a component for flexible display, solar cells or sensor.

Summary of Work for June, 2005-December, 2007

Among several CNT samples we tested, the best performance result we have achieved is with metallic SWNT (m-SWNT) coated on PEN (poly-ethylene-naphthalate) transparent composite film: it gave conductivity of 130Ω/sq with 80% transmittance at 400-700nm wavelength range. In contrast, current commercially available single side inorganic, brittle ITO coated PET film gave 88Ω/sq with 80% transmittance. Our sample mentioned above was prepared with double side coating using a dipping method. Once one side is coated, it is estimated that transmittance can probably reach close to a 90% level. Based on this assumption, we can draw a conclusion that one side m-SWNT coated substrate is near to meet with requirements of several electronic applications such as EMI, display, touch screen and others. There are two possible reasons why m-SWNT gives excellent performance: 1. metallic SWNT has intrinsically higher conductivity than un-separated one has, and 2. no use of surfactant in preparing dispersion will help to reach high conductivity since surfactant itself is an insulator. We discovered that NMP (n-methyl-

pyrolidone) solvent disperses m-SWNTs well with no use of surfactant. Besides achieving high electrical and optical performance with m-SWNT use, we also found that CNTs adhere well to PEN (poly-ethylene-naphthalate) film surface and it passes tape adhesion test. The m-SWNT, the best one we have scouted, was separated and kindly provided by Prof. Sun of Clemson University. PEN film, the best film substrate we scouted, is being produced by DuPont-Teijin. The m-SWNTs provided by Prof. Sun were separated from SWNTs synthesized by arc discharge method. Although m-SWNT separated from SWNTs synthesized by laser ablation method can give better results than m-SWNT separated from SWNTs made by arc discharge synthesis, we decided at this moment not to pursue since there is no commercial supplier. Instead, we are pursuing for the separation of m-SWNT from Hipco SWNTs since it is commercially available.

We fabricated a few sample electronic devices such as PLEDs, solar cell and methanol sensor with our transparent flexible SWNT coated substrate. The sample devices show a promising lead that SWNT coated substrate as a component has potential to be used for the fabrication of flexible electronic devices.

Introduction:

Carbon nanotubes (CNTs) are the material of ever-increasing concern due to their excellent electronic and physicochemical properties [1]. Currently, a lot of research has been focused towards their applications for use in chemical and biological sensors as well as their use in optoelectronic devices [2]. One of the major challenges is the construction of flexible electronic

devices. Transparent and electrically conductive materials such as oxide semiconductors - indium tin oxide (ITO) can be used for versatile applications for flexible electronic devices such as display, solar cells and sensor. Currently ITO has short supply and is becoming very expensive. Besides the concern on supply & price, ITO is an inorganic, brittle material so it has a limit to be used with flexible substrate. Thus, transparent, flexible and conductive coating composite built with carbon nanotubes may offer an alternate solution with flexibility needed for a wide variety of applications, especially, flexible displays, solar cells and sensors [3-4].

Experimental:

1-*Preparation of coated substrates:*

An average of 15-20mg sample of m-SWNT was dispersed in NMP solvent without using any surfactant. The mixture was then sonicated with a bath sonicator for 1 hour. The CNTs dispersed solution was added to a beaker having 100ml of NMP (n-methyl-pyrolidone). When we prepared dispersion with Hipco SWNT, we used the following method. An average of 15-20mg sample was dispersed in methanol without using any surfactant. The mixture was then sonicated with a probe sonicator for 25 min with pulse at 0.5 second cycle at power output of 35-45%. The CNTs dispersed solution made was added to a beaker with 100ml of methanol. The solution was kept under bath sonication while dipping a piece of PET or PEN. UV-Vis spectra were recorded using PERKIN ELMER between 400 and 700 nm. The sheet resistance (Ω/sq) measurement was carried out using 4-probes configuration with Keithley 2000 instrument.

2- Contact Angle measurement

Water contact angle with PEN and PET film was measured using a manual goniometry of

Rame-hart Inc., model # 50-00-115.

3-Preparation of PLED device:

Purified HiPco SWNTs were used to make the first coating on PET. poly(3,4-ethylenedioxythiophene) – poly(styrenesulfonic acid) (PEDOT-PSS) (Baytron P) was spin coated onto the SWNT film at 2500rpm for 1min, followed by drying at 80 C for 1h. Next a 0.4 wt % poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene-vinylene (MEH-PPV) solution in toluene was spin coated at 1000 rpm to form a uniform coating of the light emitting polymer over the substrate. A double layer of cathode contact consisting of Ca and Al with thicknesses of about 100 Å and 2000 Å respectively were deposited by an E-beam evaporator through a shadow mask.

4-Preparation of solar cell:

a- Preparation of natural organic dye from parsley:

Parsley leaves were chopped on fine pieces then dissolved in acetone. The mixture was stirred for 3 hours. The extract was then filtered and UV-Vis spectra were taken by UV-vis 1601PC Shimadzu. The absorbance spectra of the dye (Figure 7) showed the presence of two intense peaks at 433nm and 662nm.

b- Preparation of solar cell:

PET coated SWNT substrate was prepared. TiO_2 nanoparticles with particle size 40-60 nm were purchased from Degussa. Polyaniline nanofibers were synthesized using a method developed by our group. Pani: TiO_2 (1/1) films were spin coated on PET/SWNT substrate.

3-Preparation of methanol sensor:

Purified HiPco SWNTs were used to make the fist coating on PET substrate. Platinum nanoparticles were synthesized using micro-emulsion technique and then deposited on this film. Electrochemical measurements were conducted by cyclic voltammetry (CV) using Pt-CNT-PET as working electrode. The electrolyte was a solution of 8% of methanol in 0.5M H_2SO_4.

Result and Discussion:

Among many CNT samples we tested, the best performance result we have achieved is with metallic SWNT (m-SWNT) coated on PEN (poly-ethylene-naphthalate) composite film: It gave conductivity of 130Ω/sq with 80% transmittance at 400-700nm wavelength range. See Tables 1. Among the purified SWNT samples, we found that SWNT from laser ablation is the best, that from Hipco process is the second best and the one from arc discharge the last as shown in Table 2. The m-SWNT coated sample was prepared with double side coatings using a dipping method. Due to the shortage of m-SWNT supply, we were not able to coat one side by using spin coating method whose method requires more volume of coating materials. Once one side is coated, it is estimated that transmittance can probably reach a 90% level or close to it. Table 3 shows that once you clean one side, the transmittance went up so if we clean one side of the 80% transmittance sample made with m-SWNT, it can probably go up about 10%. Based on this assumption, we can draw a conclusion that one side m-SWNT coated substrate can with the requirements of several electronic applications such as EMI, display, touch screen and others as shown in Figure 1. There are two possible reasons why m-SWNT gave good performance: 1. metallic SWNT has intrinsically higher conductivity than un-separated one has, and 2. no use of surfactant for m-SWNT dispersion will help to reach high conductivity since surfactant itself acts as an insulator. We discovered that NMP (n-methyl-pyrolidone) solvent disperses m-SWNTs

well with no use of surfactant (Figure 2). It is known in the literatures [3-4] that they used a surfactant (Triton-X or SDS) to prepare SWNT dispersed solution and coated SWNT on a film with it and then removed surfactant using an organic solvent or strong acid to increase conductivity. Surprisingly, we observed that m-SWNTs are not dispersible in Triton-X 100 or SDS in DI water while un-separated SWNTs are dispersible well with the surfactants in DI water as shown in Figure 2. (This is an interesting observation that deserves a research in the future.). This new discovery will definitely enable us to simplify overall processes from m-SWNT dispersion preparation to m-SWNT coated substrate since we do not need not only to use surfactant to prepare m-SWNT dispersion but also to remove the surfactant from the coated substrate contrast to their methods reported in the literatures. The residual surfactant if left in coated film will give adverse effect on conductivity and chemical stability over device's life time operation conditions. We found that PEN film gives better results that PET film. See Table 3. We also found that CNT coated on PEN film gives excellent adhesion and passes tape adhesion test besides giving good electrical & optical performance. In order to understand adhesion mechanism, we tested hydrophobic property difference between surfaces of PEN & PET film by water contact angle measurement. We detected that PEN film gave a contact angle of 65 while PET film a contact angle of 45 degree. This result concludes that PEN film surface is more hydrophobic than PET film surface. Since CNT has hydrophobic property, it is more compatible with PEN surface vs. PET surface. PEN film contains naphthalene rings and PET film benzene rings so it can be anticipated that PEN, having more aromatic rings, should have higher hydrophobicity than PET has. In studying CNT coating on substrate, we discovered that CNTs coating on flexible substrate can be drawn into fibers or yarns. Based on this discovery, we have submitted a proposal to AFOSR in 2007. This fascinating result along with adhesion study has

led us to investigate further to study its fundamental adhesion mechanism. From the mechanism study, we believe we will be able to improve our current best result further hopefully towards the performance level (88Ω/sq with 80% transmittance) of ITO single side coated plastic substrate. The m-SWNT, we have scouted, was separated and kindly provided by Prof. Sun of Clemson University [5]. The m-SWNT sample provided was separated from SWNTs synthesized by arc discharge method. Although m-SWNTs from laser ablation method, once separated, will probably give better results than what we have obtained with m-SWNT from arc discharge synthesis which can be speculated from the results shown in Table 2, we decided not to seek for the separation of m-SWNT from SWNT made from laser ablation method since there is no commercial supplier. Instead, we are to seek for the separation of m-SWNT from commercially available Hipco SWNTs. In addition, our data show that between un-separated SWNT made by arc discharge method and that by Hipco process, Hipco SWNT is better based on our conductivity and transmittance test results as shown in Table 2. But, before we undertake the separation of m-SWNT from Hipco SWNT sample, we first want to check batch-to-batch reproducibility of its quality since the reproducibility is an important factor for commercial development for flexible devices. Preliminary data indicate as shown in Table 4, its batch-to-batch quality consistency varies but it may be acceptable: Three batches out of four batches are close in terms of quality considering both transmittance and conductivity. Thus, we now are in the process of setting up a separation unit.

ITO has been the preferred choice for conductive coatings for decades. However, ITO has some limitations: the films made with ITO are brittle due to inorganic material. Therefore, it is a great concern for flexible electronic device applications. It is known that CNTs can resist mechanical

test such as bending or crumpling with little loss of conductivity. Our test with SWNT coated PEN confirmed that it showed a minute increase sheet resistivity even after severe bending and crumpling abuse test. Figure 3 shows our test results of conductivity change vs. degree of bending done with our SWNT coated PEN and commercially available sample of ITO coated PET. It clearly shows that our SWNT coated PEN sample is more flexible, and this positively leads to potential opportunity of SWNT use for flexible electronic devices.

To know if we can fabricate flexible electronic devices with SWNT coated film, we made proto-types of three devices and their performance results are as shown in Figures 4-8: PLEDs (polymer LEDs) device, a solar cell and methanol sensor. The PLEDs device was fabricated by using SWNTs coated film having 275 Ω/sq and 79% transmittance (Figure 4). We demonstrated that PET/SWNT flexible sheet can be used as anode for PLEDs. The non-optimized PLED device exhibited low turn-on voltages (~5 V) within acceptable range as shown Figure 5 although the light output is still low.

A dye sensitized solar cell made by coating pigments in an extract from parsley leaves on a nanocrystalline film of TiO_2 has been tested (Figure 6). The output characteristics preliminarily obtained from this device show measurable photo-voltage without any device optimization (Figure 7). The result achieved is encouraging, especially taken together with the nature of dye and the SWNT coated film's flexibility.

The electrochemical performance of the Pt-SWNT/PET film has also been investigated by cyclic voltammetry in 0.8% CH_3OH + 0.5 M H_2SO_4 solutions, and the typical cyclic voltammogram is shown in Figure 7. Two oxidation peaks, which are related to the oxidation of methanol and the corresponding intermediates produces during methanol oxidation, can be observed at 0.75V and 0.57V respectively. These peak potentials are in good agreement with literature values [6].

Conclusions:

In summary, using m-SWNT and PEN film, we have achieved a conductivity of 130Ω/sq with 80% transmittance at 400-700nm wavelength range. This sample was prepared with both sides coating using a dipping method. Once one side is coated, it is estimated that transmittance can probably reach close to a 90% level which can meet with requirement of several flexible electronic devices as shown Figure 1. We have also demonstrated the ease and simplicity of fabrication of a few devices using electronically conductive films of SWNTs on flexible substrates prepared without using any surfactant. The combination of high optical transparency, low sheet resistance and robust flexibility could lead to important advances in the design and development of flexible electronic devices and probably in the future replace commercial ITO films. Experimental results showed that the film performance strongly depends on the carbon nanotube qualities such as purity, length, defects, chirality, and the degree of dispersion.

Future Work:

We discovered that CNTs coated on flexible film can be drawn into fibers and yarns. We have submitted to AFOSR to do further research to develop new fabrication process of CNT fiber/yarn. We also want to study how much we can further improve conductivity & transmittance with m-SWNT separated from Hipco SWNTs. Lastly, a visitor form the major displayer stated that one of the key challenges for CNT coated flexible film for successful commercial application is CNT's adhesion on flexible substrate so we would like to continue our study to uncover fundamentals with AFOSR funding.

Table 1. Effect of Chirality of SWNTs and number of coatings vs. Transmittance and Sheet Resistance when coated on PEN substrate

Sample	One coating		Double coatings		Triple coatings	
	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)
Mixture	78	167K	72	61K	69	56K
Semi-conducting	82	1.90K	79	0.95K	75	493
Metallic	85	403	82	262	80	130

Substrate: PEN (polyethylene naphthalate): ca. 95% transmittance with no CNTs coating.
Sheet resistance: Not measurable (too high).

Table 2. Different SWNTs Samples vs. Transmittance & Conductivity

Sample	One coating		Double coatings		Triple coatings	
	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)
As-synthesized HiPco	80	6.93K	75	2.85K	72	883
Purified HiPco	72	1.90K	70	0.95K	65	493
Purified laser	75	1.3K	72	974	69	275
Zyvex SWNT	81	-	79	45K	72	27K
ASA-100F	79	380K	72	158K	69	100k
Purified SWNT ex. arc-discharge	78	167K	72	61K	70	56k

Control: PET (polyethylene terephtalate):
Transmittance: 85%
Sheet resistance: Not measurable (too high).

Table 3. Transmittance at 550nm after one side cleaned (purified Hipco on PET)

sample	before	after	ΔT%
1	73.90	86.98	17
2	71.14	85.28	20
3	61.84	80.02	29
4	69.92	73.79	5
5	71.12	84.56	19
6	65.60	85.44	30

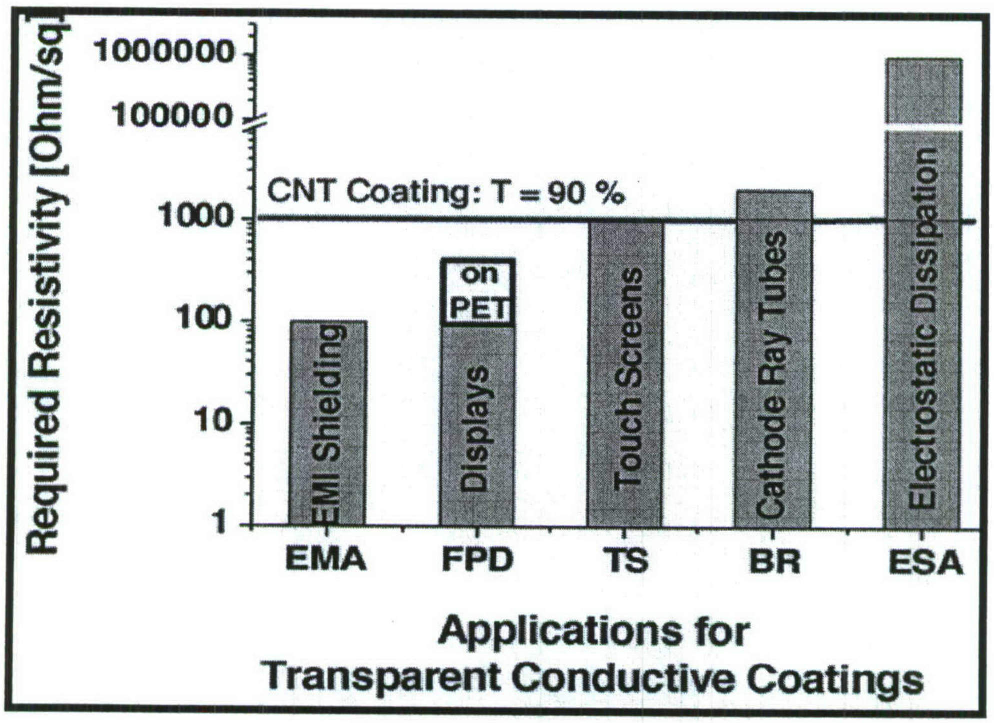
Table 4. PET and PEN vs. Transmittance and Conductivity

Sample	One coating		Double coatings		Triple coatings	
	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)
PET	79	6.93K	75	2.85K	70	883
PEN	85	1.90K	82	0.95K	80	493

Table 5. Purified Hipco: Batch-to-batch Variation vs. Transmittance & Conductivity

Sample	One coating		Double coatings		Triple coatings	
	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)	T%	Rs(Ω/sq)
Batch P0175	84	$25x\ 10^3$	81	$1.4x10^3$	79	125
Batch P0288	82	$19x\ 10^3$	80	$0.95x10^3$	80	493
Batch Q0697	85	$35x\ 10^3$	83	$1.02x10^3$	79	265
Batch S8206	84	$21x\ 10^3$	82	$1.62x10^3$	80	196

Figure 1. Applications for transparent conductive CNT coating

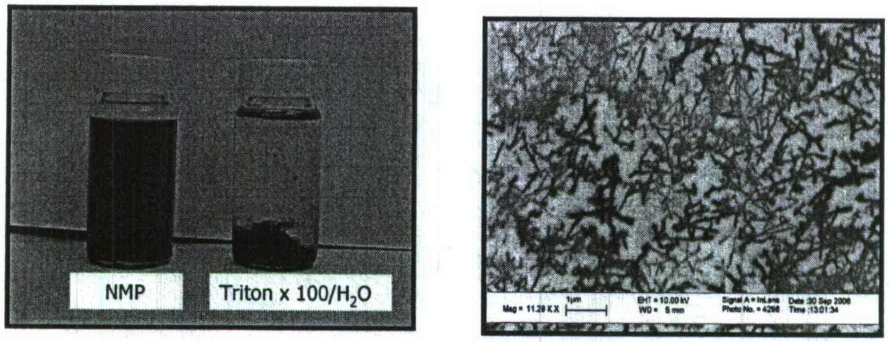


EMI: electromagnetic interferences; FPD: flat panel display; TS: touch screen

EMS: electromagnetic shielding for cathode ray tubes; ESD: electrostatic dissipation.

M. Kaempgen *et al.*, *Synth. Met.* 135 **(2003)**, p. 755.

Fig. 2. Metallic SWNT: a) Dispersion Test & b) SEM Picture



a) **Metallic SWNTs Dispersion: NMP & Triton x 100/H2O**

b) **SEM of metallic SWNT coated on PEN substrate**

Figure 3. Flexibility Test by 2 probe resistance measurement: SWNT/PET vs. ITO/PET

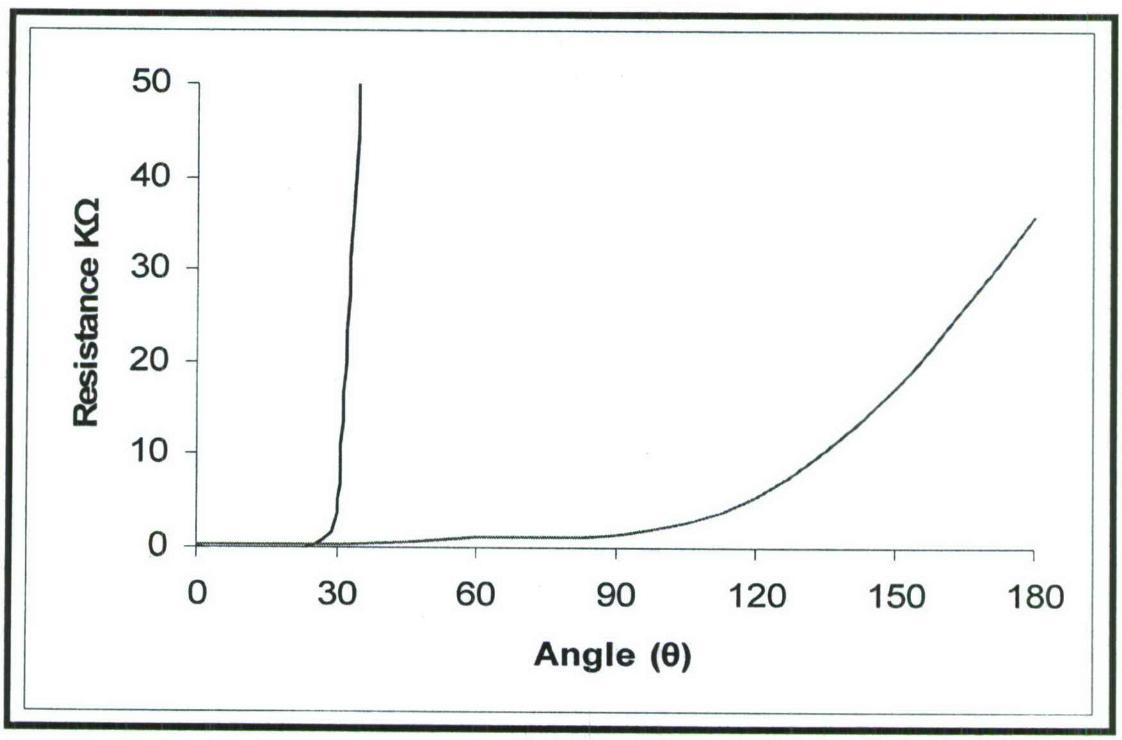


Figure 4: (a) Picture of SWNTs coated on PET & (b) assembled PLED device

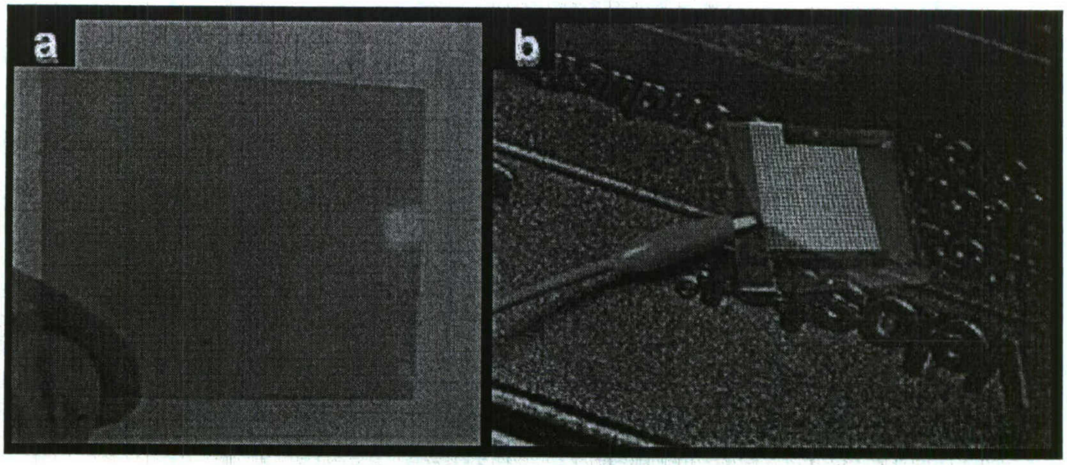


Figure 5: I-V Characteristic Curve of PLED Device.

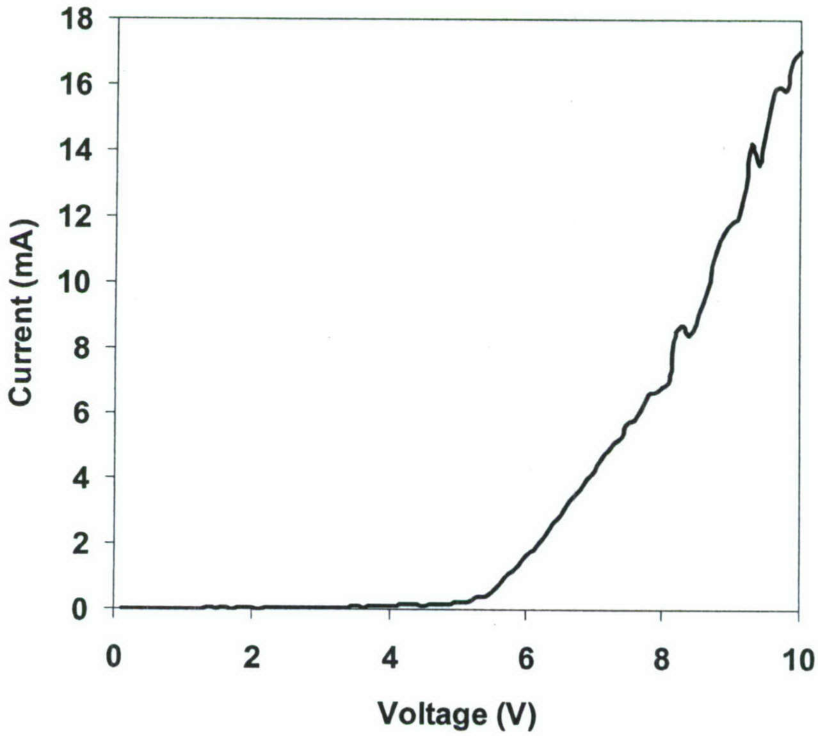
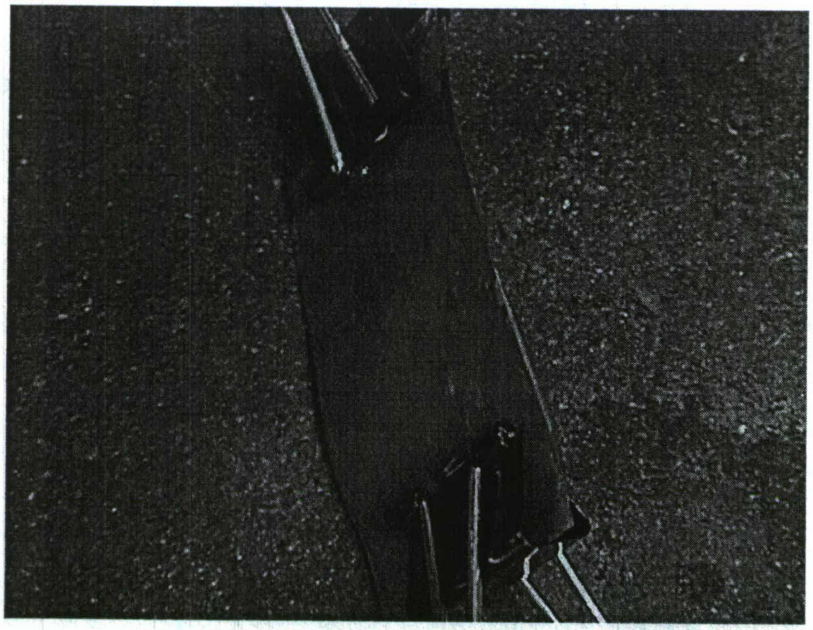


Figure 6. Solar Cell



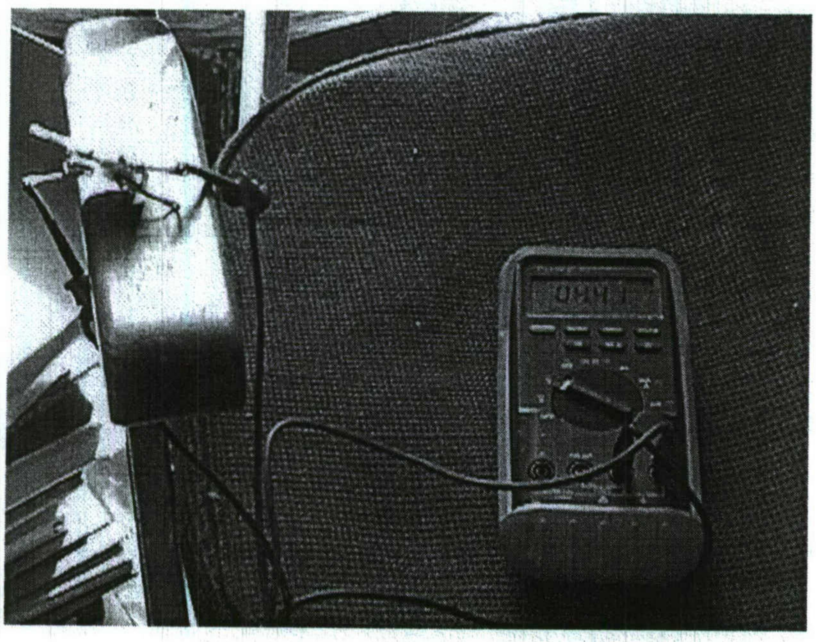
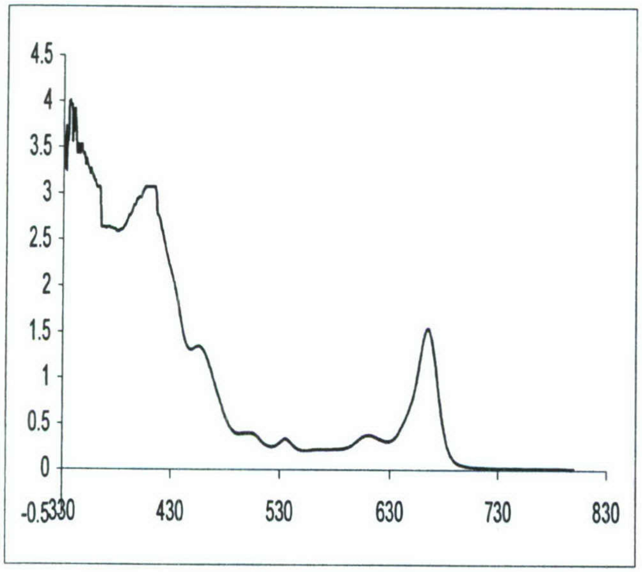


Figure 7. Output characteristics of a solar cell

Absorbance spectrum of parsley



Photovoltaic Curve

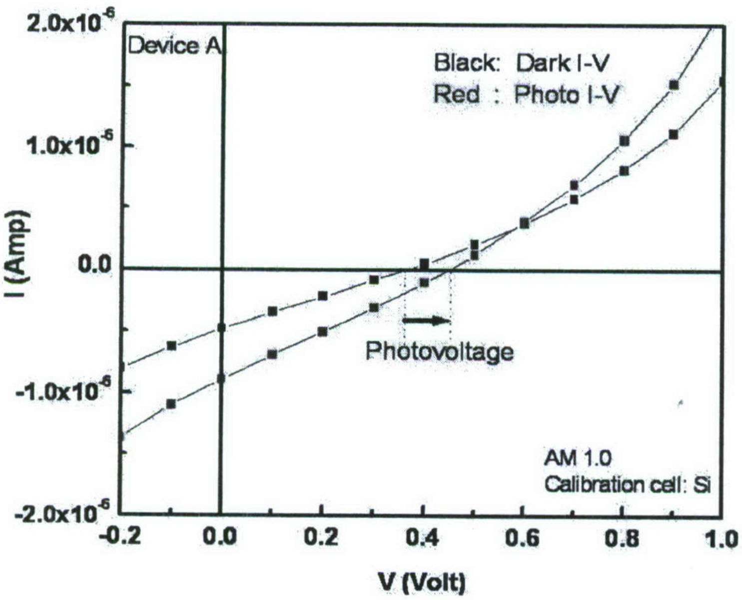
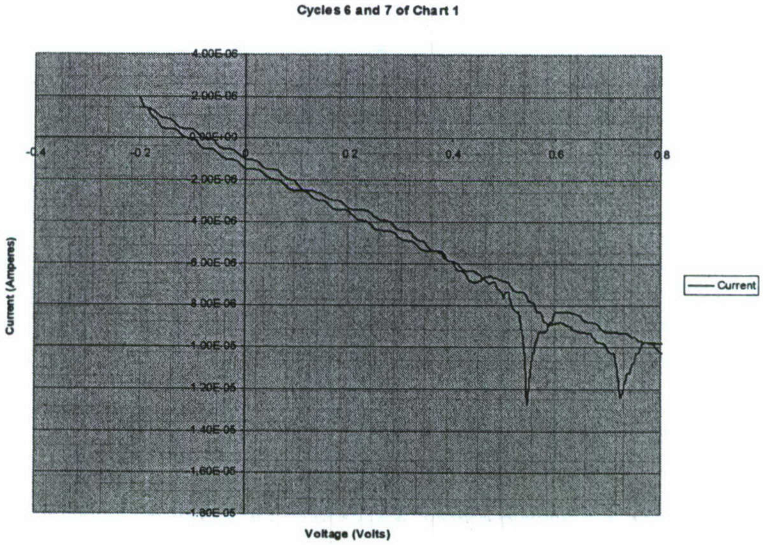


Figure 8: Cyclic Voltammogram. Measured with Pt/Purified Hipco SWNTs Coated on PET Electrode in 8% Methanol + 0.5M H_2SO_4



References:

[1] W. A. de Heer, A. Châtelain, D.G. Ugarte, A carbon nanotube field-emission electron source, *Science,* 1995, 270, 1179-1180.

[2] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, Carbon nanotubes-the route toward applications, *Science*, 2002, 297, 787-792.

[3] N. Saran, K. Parikh, D. S. Suh, E. Munoz, H. Kolla, and S. K. Manohar, Fabrication and characterization of thin films of single-walled carbon nanotube bundles on flexible plastic substrates, *J. Am. Chem. Soc.* 2004,126, 4462-4463

[4] Hong-Zhang Geng, Ki Kang Kim, Kang Pyo So, Young Sil Lee, Youngkyu Chang, and Young Hee Lee . Effect of Acid Treatment on Carbon Nanotube-Based Flexible Transparent Conducting Films *J. Am. Chem. Soc.* 2007, 129, 7758-7759

[5] Wang Wei; Fernando K A Shiral; Lin Yi; Meziani Mohammed J; Veca L Monica; Cao Li; Zhang Puyu; Kimani Martin M; Sun Ya-Ping Metallic single-walled carbon nanotubes for conductive nanocomposites. *Journal of the American Chemical Society* (2008), 130(4), 1415-9

[6] Z. He, J. Chen, D. Liu, H. Tang, W. Deng, Y. Kuang, *Materials Chemistry and Physics*, 2004, 85, 396-401.